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SYNTHESIS OF 4,5-DIHYDROFURAN DERIVATIVES BY THE REACTION OF ACETOACETIC ESTER WITH CONJUGATED ALKENYNES*

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The regiochemistry of the reaction of acetoacetic ester with vinylacetylene, isopropenylacetylene, and vinylisopropenylacetylene in the presence of the manganese acetate/copper acetate oxidative system was studied. Derivatives of furan and 4,5-dihydrofuran were obtained as a result of oxidative cyclization of intermediate radicals that contain unsaturated groups in the α position. Data from the IR, UV, PMR, ^{13}C NMR, and mass spectra of the synthesized compounds are presented.

We have recently studied the reaction of conjugated alkenes with acetylacetone in the presence of the manganese(III) acetate/copper(II) acetate oxidative system [2]. We showed, in particular, that the reaction of the acetylacetonyl radical with vinylacetylene proceeds nonregioselectively and that the intermediate reaction particles, which contain unsaturated groups in the α position, are stabilized exclusively via a cyclization pathway that leads to the formation of dihydrofuran and furan derivatives.

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*Communication 75 from the series "Reactions of Unsaturated Compounds." See [1] for Communication 74.

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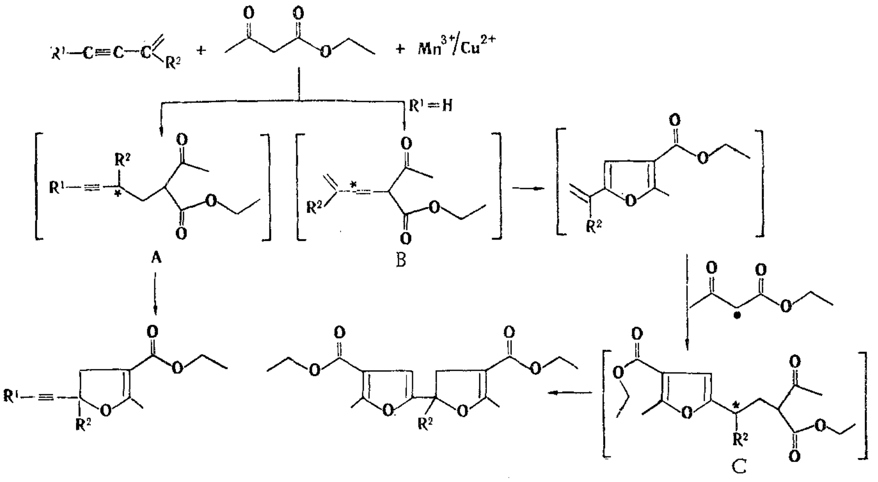
In the present research we subjected conjugated alkenynes, viz., vinylacetylene, isopropenylacetylene, and vinylisopropenylacetylene, to the investigated reaction in the role of unsaturated components with acetoacetic ester acting as the carbonyl component. We undertook two tasks in our research: to investigate the regiochemistry of the investigated reaction and to obtain new experimental data on the pathways of stabilization of the intermediate particles, which contain unsaturated groups in the α position.

The reaction of vinylacetylene with acetoacetic ester in acetic acid at 70-75°C leads to two principal reaction products, viz., I and II, which were isolated by means of column chromatography. Similar compounds were previously obtained in the reaction of vinylacetylene with acetylacetone, and the pathways via which they are formed were discussed in detail in [2].

It was shown by a special experiment that the action of acetoacetic ester on I under the reaction conditions does not lead to II. In other words, products I and II are formed as a result of parallel rather than consecutive processes.

The ratio of I and II determined from the PMR spectrum of the crude mixture is 1:1.2, which constitutes evidence for the commensurable participation of the vinyl and ethynyl groups in the reaction. As compared with the reaction of vinylacetylene with acetylacetone [2], the value obtained constitutes evidence for the relatively greater participation of the vinyl group in the reaction.

The reaction of isopropenylacetylene with acetoacetic ester under the same conditions leads to similar products III and IV, which were isolated by means of column chromatography. Their ratio, determined from the PMR spectrum of the crude mixture, is 8.4:1, i.e., a considerable change in the regiochemistry of the reaction occurs as compared with the reaction of vinylacetylene. The presence of a methyl group, which increases the stability of the propargyl radical as compared with the dienyl radical, is responsible for primary reaction at the double bond of the molecule. This increase in regioselectivity makes the reaction a preparative method for the synthesis of III.



I $R^1=R^2=H$; II $R^2=H$; III $R^1=H$, $R^2=CH_3$; IV $R^2=CH_3$; V R^1= vinyl, $R^2=CH_3$;
VI R^1= isopropenyl, $R^2=H$

The reaction of vinylisopropenylacetylene with acetoacetic ester takes place primarily at the isopropenyl group and leads to a mixture of isomeric V and VI. Their ratio in the crude mixture, determined by gas–liquid chromatography (GLC), is 9:1. The rather high regioselectivity of the reaction, which constitutes evidence for the significant contribution of the methyl group to stabilization of the propargyl radicals, makes this a preparative method for the synthesis of V.

An absorption band of a cyclic β-alkoxyacrylic chromophore at 255-258 nm is observed in the UV spectra of I-V. The absorption band of a cyclic β-alkoxyenone chromophore is found at 275-280 nm [2], i.e., replacement of the methyl group by an ethoxy group leads to a 20 nm hypsochromic shift of the absorption band. The absorption band of a carbethoxy group is observed at 1705-1712 cm^{-1} in the IR spectra of I-V, while the absorption band of a dihydrofuran ring is observed at 1645-1660 cm^{-1}. These data constitute evidence that conjugation significantly lowers the frequency of absorption of the carbethoxy group but has virtually no effect on the frequency of the absorption of the double bond of the dihydrofuran ring. It should be noted that in the case of 3-acetyl-4,5-dihydrofurans conjugation lowered the frequencies of the absorption of both the carbonyl group and the double bond identically, and splitting was observed for the latter [2]. Splitting is observed in the spectra of I-V only for the carbethoxy group in V, and the absorption frequency is lowered somewhat (1698, 1685 cm^{-1}). Long-range spin-spin coupling (J = 1.6 Hz) between the methylene group of the dihydrofuran ring and the methyl group attached to the double bond is observed in the PMR spectra of I-V, and the protons of the methylene group of the dihydrofuran ring in I, III, and V are magnetically nonequivalent. It has been previously noted [2] for two of the compounds that when a 2-furyl group is present in the 5 position of the dihydrofuran ring, the protons of the methylene group are magnetically equivalent. In this case, as expected, the protons of the methylene group in II proved to be magnetically equivalent, whereas the corresponding protons in IV were magnetically nonequivalent.

The formation of furan and dihydrofuran rings in the reactions of conjugated alkenynes with acetoacetic ester indicates that hypothetical intermediate particles of the A, B, and C type are stabilized exclusively via one of the alternative paths, viz., via cyclization. The question as to whether the corresponding radicals undergo direct oxidative cyclization under the influence of copper(II) acetate or undergo prior oxidation to carbonium ions should be the subject of a separate study.* However, common to structures A, B, and C is the fact that the carbon atoms that have free valences (designated by asterisks) contain unsaturated groups in the α position, which makes the intermediate particles (radicals or carbonium ions) more stable as compared with the saturated analogs owing to conjugation. The eight intermediate particles represented by types A, B, and C, together with the five structures presented in [2], indicate that the above-noted relationship between the structure of the intermediate particles and their stabilization pathway is rather general in character.

It should be noted that when acetyl and carbethoxy groups were present in the molecule, cyclization in all cases took place at the acetyl group.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in carbon tetrachloride were obtained with a Perkin-Elmer R12B spectrometer with an operating frequency of 60 MHz, while the ^{13}C NMR spectra were obtained with a Bruker HX-90 spectrometer (22.64 MHz); the chemical shifts are presented in the δ scale relative to tetramethylsilane (TMS). The IR spectra of thin layers of the pure substances were obtained with a UR-10 spectrometer. The UV spectra of solutions of the compounds in ethanol were obtained with a Specord UV-vis spectrophotometer. The mass spectra were recorded with a DS-50 spectrometer with direct introduction of the samples into the ionization region at an input temperature of 20°C and an ionizing voltage of 70 eV. Gas-liquid chromatography (GLC) was carried out with a Tsvet-104 chromatograph with a catharometer, a glass column (2 m by 3 mm) packed with 5% SE-30/Chromaton N-AW-DMCS (0.200-0.250 mm), and helium as the carrier gas. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with detection by iodine vapors.

The constants of I-V are presented in Table 1.

3-Carbethoxy-2-methyl-5-ethynyl- and 3-Carbethoxy-2-methyl-5-(3-carbethoxy-2-methyl-5-furyl)-4,5-dihydrofurans (I, II). A 2.64-g (0.01 mole) sample of $Mn(OAc)_3 \cdot 2H_2O$ and 2.56 g (0.02 mole) of acetoacetic ester were added to a solution of 0.15 g (0.7 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 6.5 ml of acetic acid, and 1.0 g (0.02 mole) of vinylacetylene in a nitrogen atmosphere was passed into the mixture at 70-75°C until the brown coloration vanished (15 min). The mixture was cooled, and the precipitated $Mn(OAc)_2$ was removed by filtration. The filtrate was diluted with 10 ml of water and extracted with ether (two 15-ml portions). The ether extract was washed with Na_2CO_3 solution and water and dried with Na_2SO_4, and the ether was evaporated *in vacuo* to give 1.97 g of a crude mixture containing, according to TLC, two principal reaction products, together with excess acetoacetic ester. The individual compounds were isolated by chromatography with a column (with an inner diameter of 2 cm) filled with 50 g of

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*The reaction of alkyl radicals with copper(II) acetate does not necessarily proceed through the formation of a carbonium ion [3]. It is therefore preferable to designate the cyclization reaction as oxidative cyclization of the corresponding radicals under the influence of copper(II) acetate.

TABLE 1. Constants of I-V

Compound	bp, °C (pressure, hPa)	n_D^{20}	R_f*	GLC, °C, ml/min, retention t (min)	Found, %		Empirical formula	Calc., %	
					C	H		C	H
I	75 (2,6)	1,4790	0,48	132, 30, 15,3	66,1	7,2	$C_{10}H_{12}O_3$	66,6	6,7
II	155—173 (1,3)	1,5100	0,40	250, 50, 5,7	62,5	6,8	$C_{16}H_{20}O_6$	62,3	6,5
III	73 (1,3)	1,4780	0,55	142, 25, 11,1	67,7	8,1	$C_{11}H_{14}O_3$	68,0	7,7
IV	—	—	0,49	—	63,5	7,1	$C_{17}H_{22}O_6$	63,4	6,8
V	97—98 (1,3)	1,5025	0,72	172, 35, 11,3	70,8	7,3	$C_{13}H_{16}O_3$	70,9	7,3

*In hexane—ether (1:1) for I-IV, and in ether for V.

SiO_2 (Woelm, 40-100 μm) by elution with hexane—ether (5:1) (the overall volume of eluent was 240 ml) to give 85 mg (9%) of I and 136 mg (13%) of II.

IR spectrum for I: 3320 (≡C—H), 2135 (C≡C), 1705 ($COOC_2H_5$), and 1652 cm^{-1} (C═C). UV spectrum, λ_{max} (log ε): 255 nm (3.96). PMR spectrum: 1.18 (3H, t, 3-$COOCH_2CH_3$), 2.10 (3H, t, 2-CH_3), 2.52 (1H, d, ethynyl H), 2.98 (2H, center of an AB system, each line a dq, CH_AH_B), 4.08 (2H, q, 3-$COOCH_2CH_3$), and 5.10 ppm (1H, ddd, 5-H), $J_{H_A-H_B}$ = 14.0, $J_{CH_3-CH_2}$ = 7.0, $J_{5\text{-}H-H_A}$ = 8.4, $J_{5\text{-}H-H_B}$ =10.2, $J_{5\text{-}H-H\text{-}ethynyl}$ = 2.2, and $J_{2\text{-}CH_3-H_{A(B)}}$ = 1.6 Hz. ^{13}C NMR spectrum: 13.60 (CH_3, q, J = 129.5 Hz), 14.26 ($COOCH_2CH_3$, q, J = 126.5 Hz), 59.28 ($COOCH_2CH_3$, tq, J = 147.1, J = 4.4 Hz), 75.20 (C≡CH, dd, J = 252.9, J = 2.9 Hz), 81.83 (**C**≡CH, m), and 164.60 ($COOCH_2CH_3$, s); carbon atoms of the dihydrofuran ring: 37.32 (C_4, t, J = 136.8 Hz), 69.93 (C_5, d, J = 155.9 Hz), 101.45 (C_3, m), and 166.55 ppm (C_2, m). Mass spectrum: M^+ 180.

IR spectrum for II: 3135 (furan ring C—H); 1725, 1710 ($2COOCH_2CH_3$); 1655 (dihydrofuran ring C═C); 1622, 1590 cm^{-1} (furan ring C═C). PMR spectrum: 1.26 and 1.32 (3H and 3H, t and t, ($2COOCH_2CH_3$); 2.16 (3H, t, dihydrofuran ring 2-CH_3), 2.58 (3H, s, furan ring 2-CH_3), 3.10 (2H, dq, CH_2), 4.16 and 4.28 (2H and 2H, q and q, $2COOCH_2CH_3$), 5.48 (1H, t, 5-H), and 6.65 ppm (1H, s, furan ring H), $J_{CH_3-CH_2}$ = 7.0, $J_{CH_3-CH_2}$ = 9.8, $J_{2\text{-}CH_3\text{-}CH_2}$ = 1.6 Hz. Mass spectrum: M^+ 308.

Products I and II can also be isolated by distillation. A 19.4-g sample of the crude mixture was distilled, and the fraction with bp 80-175°C (1.3 hPa) was collected to give 3.3 g of a mixture of I and II. Redistillation gave 1.1 g of I (78% purity according to GLC) and 1.4 g of II (83% purity according to GLC).

The ratio of I and II in the crude mixture was determined from the PMR spectrum by weighing the signals at 5.10 ppm for I and at 5.48 and 6.65 ppm for II recorded at a sweep of 1 Hz (4.5 mm). The average value of the I:II molar ratio was 1:1.2.

3-Carbethoxy-2,5-dimethyl-5-ethynyl- and 3-Carbethoxy-2,5-dimethyl-5-(3-carbethoxy-2-methyl-5-furyl)-4,5-dihydrofurans (III, IV). Similarly, 0.2 g (0.9 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 10 ml of acetic acid, 3.9 g (0.015 mole) of $Mn(OAc)_3 \cdot 2H_2O$, 3.8 g (0.03 mole) of acetoacetic ester, and 1.2 g (0.018 mole) of isopropenylacetylene gave 3.65 g of a crude mixture containing, according to TLC data, two principal reaction products, together with excess acetoacetic ester. The individual compounds were isolated by means of column chromatography under conditions identical to those in the preceding experiment, as a result of which, 765 mg (51%) of III and 127 mg (6%) of IV were obtained.

IR spectrum for III: 3300 (≡C—H), 2130 (C≡C), 1710 ($COOC_2H_5$), and 1655 cm^{-1} (C═C). UV spectrum, λ_{max} (log ε): 255 nm (3.94). PMR spectrum: 1.22 (3H, t, 3-$COOCH_2CH_3$), 1.62 (3H, s, -CH_3), 2.15 (3H, t, 2-CH_3), 2.54 (1H, s, ethynyl H), 3.00 (2H, center of an ABX_3 system, CH_AH_B), and 4.13 ppm (2H, q, 3-$COOCH_2CH_3$), $J_{H_A-H_B}$ = 14.4, $J_{CH_3-CH_2}$ = 7.0, $J_{2\text{-}CH_3-H_{A(B)}}$ = 1.6 Hz. Mass spectrum: M^+ 194.

IR spectrum for IV: 3140 (furan ring C—H); 1725, 1712 ($2COOCH_2CH_3$); 1658 (dihydrofuran ring C═C); 1622, 1585 cm^{-1} (furan ring C═C). UV spectrum, λ_{max} (log ε): 204 (3.76) and 255 nm (3.84). PMR spectrum: 1.23 and 1.30 (3H and 3H, t and t, $2COOCH_2CH_3$), 1.63 (3H, s, 5-CH_3), 2.14 (3H, t, dihydrofuran ring 2-CH_3), 3.00 (2H, center of an ABX_3 system, CH_AH_B), 4.10 and 4.22 (2H and 2H, 2H, and q, $2COOCH_2CH_3$), and 6.47 ppm (1H, s, furan ring H), $J_{H_A-H_B}$ = $J_{CH_3-CH_2}$ = 7.0, and $J_{2\text{-}CH_3-H_{A(B)}}$ = 1.6 Hz. Mass spectrum: M^+ 322.

Compound III can be isolated in 48% yield by distillation of the crude mixture.

The ratio of III and IV in the crude mixture, which was similarly determined from the signals at 2.54 ppm for III and at 6.47 for IV, was 8.4:1.

3-Carbethoxy-2,5-dimethyl-5-(3-buten-1-ynyl)- and 3-Carbethoxy-2-methyl-5-(3-methyl-3-buten-1-ynyl)-4,5-dihydrofurans (V, VI). Similarly, the reaction of 1.5 g (7 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 65 ml of acetic acid, 26.8 g (0.1 mole) of $Mn(OAc)_3 \cdot 2H_2O$, 26.0 g (0.2 mole) of acetoacetic ester, and 9.2 g (0.1 mole) of vinylisopropenylacetylene gave 30.1 g of a crude product containing, according to GLC data, V and VI in a ratio of 9:1. The crude mixture was distilled, and the fraction with bp 90-140°C (1.3 hPa) was collected. Redistillation gave 7.0 g (64%) of V with a purity of 94%.

IR spectrum for V: 3110 ($\equiv$C-H); 2225 (C$\equiv$C); 1698, 1685 (splitting of $COOCH_2CH_3$); 1645 (dihydrofuran ring C=C); 1610 cm^{-1} (C=C). UV spectrum, λ_{max} (log ε): 215 (3.90), 223 (3.97), 232 (3.95), and 258 nm (3.98). PMR spectrum: 1.24 (3H, t, 3-$COOCH_2CH_3$), 1.61 (3H, s, 5-CH_3), 2.16 (3H, t, 2-CH_3), 3.00 (2H, center of an ABX_3 system, CH_AH_B), 4.12 (2H, q, 3-$COOCH_2CH_3$), and 5.30-5.88 ppm (3H, vinyl group), $J_{H_A-H_B}$ = 13.9, $J_{CH_3-CH_2}$ = 7.0, $J_{2-CH_3-H_{A(B)}}$ = 1.6 Hz.

Compound VI was identical with respect to the results of GLC (retention time 15.8 min under the conditions of the GLC experiment presented in Table 1 for V) to a genuine sample obtained by a similar reaction form dimethylvinylethynylcarbinol.

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MASS SPECTRA OF cis- AND trans-4-ALKYL-3-PHENYL-3,4-DIHYDROCOUMARINS

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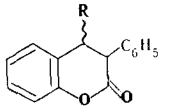
An analysis of the mass-spectrometric behavior of cis- and trans-4-alkyl-3-phenyl-3,4-dihydrocoumarins makes it possible to distinguish each of the isomers when the mass spectra of the two compounds are simultaneously present.

We have previously developed a method for the synthesis of isomeric cis- and trans-4-alkyl-3-phenyl-3,4-dihydrocoumarins [1], and we have recently determined the geometry of each of them by PMR spectroscopy [2, 3]. It seemed of interest to attempt to find the mass-spectrometric characteristics of this group of compounds, which would make it possible to identify similar geometrical isomers. For this, we studied the behavior of a series of cis and trans isomers of 4-alkyl-3-phenyl-3,4-dihydrocoumarins (Ia, b-IVa, b) under electron impact.



Ia,b-IVa,b

a = cis, b = trans
I R=C_2H_5; II R=$CH(CH_3)_2$;
III R=$C(CH_3)_3$; IV R=$CH_2C_6H_5$

An analysis of the mass spectra obtained (see Table 1) shows that the molecular ions of the investigated compounds undergo fragmentation primarily via two pathways (see Scheme 1). They either lose a substituent in the 4 position with subsequent fragmentation of the resulting F_1 fragment to give F_2 and F_3 ions, which are characteristic for the fragmentation of cou-

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